THE STOICHIOMETRY OF THE HYDRATION OF TRICALCIUM SILICATE AT ROOM TEMPERATURE. I. HYDRATION IN A BALL MILL

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When tricalcium silicate, Ca_3SiO_5, is hydrated in a ball mill, the stoichiometry of the reaction at 23° in a saturated calcium hydroxide solution is represented by the equation $2Ca_3SiO_5 + 6H_2O = Ca_3(SiO_3OH)_2{\cdot}2H_2O + 3Ca(OH)_2$. An H_2O/Ca_3SiO_5 weight ratio of 9 was used in the ball mill, and complete hydration was attained in six days. The calcium silicate hydrate produced was afwillite. The afwillite was colloidal in dimensions; most of the particles were roughly spherical and their diameter was of the order of 300 Å. The density was 2.647 ± 0.01 g./cc.; the mean index of refraction was 1.62 ± 0.01. No difference, except in the dimensions of the particles, was found between the natural mineral and artificial afwillite.

Introduction

Primarily because tricalcium silicate, Ca_3SiO_5, is one of the important constituents of portland cement, its hydration has been extensively investigated. These, as well as other investigations of the $CaO–SiO_2–H_2O$ system, were critically reviewed by Steinour.[1] Although valuable information has been gathered by several investigators, the stoichiometry of the hydration of Ca_3SiO_5 has not been settled.

When Ca_3SiO_5 is treated with solutions of lime in water, the reaction products are $Ca(OH)_2$ and calcium silicate hydrates of various compositions. At a concentration of 2 mmoles of CaO per liter, the molar ratio of CaO to SiO_2 is around 1.0 (or possibly as low as 0.8); at or near the saturation concentration the ratio is about 1.5. Taylor,[2] who made the most complete investigation of this system, designated the hydrates as calcium silicate hydrate (I) or CSH (I). Because of their similarity to the natural mineral tobermorite,[3] we shall call them tobermorites.

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(1) H. H. Steinour, *Chem. Revs.*, **40**, 391 (1947); "Proceedings of the Third International Symposium on the Chemistry of Cement," London, 1952, p. 261.

(2) H. F. W. Taylor, *J. Chem. Soc.*, 3682 (1950).

(3) G. F. Claringbull and M. H. Hey, *Mineral. Mag.*, **29**, 960 (1952).

If in a mixture of water and Ca_3SiO_5 the weight ratio of water to Ca_3SiO_5 is less than about 300, the water becomes saturated with $Ca(OH)_2$. It follows from this that unless a very large excess of water is used, the hydration takes place—or at least ends—in a saturated lime solution. Of especial importance is the hydration in saturated calcium hydroxide solution because in the hydration of portland cement lime saturation is quickly established, and thereafter the Ca_3SiO_5 component of portland cement hydrates in a saturated solution. To determine by chemical means the composition of the calcium silicate hydrate produced, the calcium hydroxide must be removed from the system, but methods so far proposed usually remove also some of the lime from the calcium silicate hydrate. Because of this, the stoichiometry of the hydration can be reliably solved only if the chemical composition and nature of the reaction products can be determined *in situ*, without disturbing the reaction system.

An *in situ* technique was used recently by Graham, Spinks and Thorvaldson,[4] who investigated the hydration of Ca_3SiO_5 and β-Ca_2SiO_4 (β-dicalcium silicate) by employing a radioactive tracer, Ca^{45}. They concluded that the calcium silicate hydrate obtained from both silicates in saturated lime solution had a molar CaO/SiO_2 ratio of 1.5. Taylor[2] and Bessey[5] found that the CaO/SiO_2 ratio of the calcium silicate hydrate *close to* lime saturation was 1.5, but both investigators believed that *at lime saturation* the CaO/SiO_2 ratio of the stable hydrate was 2.0. Our results confirm the result of Graham, Spinks and Thorvaldson for Ca_3SiO_5, and give additional information on the stoichiometry of the hydration of Ca_3SiO_5 at room temperature in saturated lime solution. We employed a number of experimental approaches, among them *in situ* techniques; the main tool for identification and quantitative determination was an X-ray diffractometer.

We investigated the hydration reaction at 23° under two conditions: (a) Ca_3SiO_5 was hydrated in a small steel ball mill; and (b) it was hydrated in the form of "paste"—imitating its presumed mode of hydration in portland cement. The former is discussed in the present paper; the latter in the second paper.

Experimental

Preparation and Hydration of Ca_3SiO_5.—We used two

(4) W. A. G. Graham, J. W. T. Spinks and T. Thorvaldson, *Can. J. Chem.*, **32**, 129 (1954).

(5) G. E. Bessey, "Proceedings of the Symposium on the Chemistry of Cements," Stockholm, 1938, p. 178.

lots of Ca_3SiO_5, designated as Ca_3SiO_5(I) and Ca_3SiO_5(II). The first lot was identical with that described by Brunauer, Hayes and Hass[6]; the second was prepared in the same manner, but it had a slightly different composition. The approximate composition of both lots was 96% Ca_3SiO_5, 3% Ca_2SiO_4 and 1% of other impurities.

Hydration was carried out in two small steel ball mills, designed by Grunwald.[7] Each mill had a capacity of about 400 cc. and was used with approximately 400 g. of steel balls of assorted sizes ($^3/_8$ to $^3/_4$″ diameter, Rockwell hardness No. 60–62). The internal dimensions of the mills were approximately 6″ diameter and 1″ width. The interior surfaces were hardened to a depth of $^1/_{32}$″ (Rockwell hardness No. 60–62); the exterior surfaces were plated with chromium. The mills were rotated at approximately 50 r.p.m. for 15 minutes of each hour.

The mills were operated in a room kept at 23 ± 0.5°. The water-to-solid weight ratio was 9. We investigated two ball-mill-hydrated batches of Ca_3SiO_5, prepared from Ca_3SiO_5 (I) and (II).

Removal of Uncombined Water.—The ball-mill slurries, at the end of the grinding period, were spooned or pipetted out of the mill and transferred to erlenmeyer flasks for freezing. The practice of freezing the slurries was adopted by Copeland and Hayes[8] to avoid sample losses owing to frothing and "boiling," which occur when the slurry is placed on the vacuum line directly. After most of the water had been removed, the samples were homogenized by thorough mixing to eliminate stratification; the rest of the adsorbed water was then removed by the procedure described by Brunauer, Hayes and Hass.[6] Drying was considered complete when the loss of water was less than 1 mg./g. of sample in two days.

All operations, to the extent possible, were conducted in a controlled atmosphere manipulation cabinet equipped with Ascarite filters, to minimize contamination of samples by CO_2.

Extraction of Calcium Hydroxide.—This was done by a modification of the method of Franke[9] for the quantitative determination of lime. A solvent mixture, made up of 60 cc. of isobutyl alcohol, 9 cc. of acetoacetic ester (ethyl acetoacetate) and 15 cc. of ethyl ether, was added to 1 g. of sample; the mixture was refluxed at 70 to 80° for three hours, filtered, and the lime in the filtrate was determined gravimetrically or volumetrically. The extraction process was then repeated on the residue; and if the filtrate obtained in the second extraction contained a sizable quantity of lime, a third extraction was performed. On some samples cold extractions were performed. Instead of refluxing the mixture, it was shaken on a rotating table for 24 hours.

Preparation of Calcium Hydroxide.—Two preparations of calcium hydroxide were used.

(a) $Ca(OH)_2$(I).—CaO was prepared by the ignition of whiting ($CaCO_3$) at 950 to 1000° for 24 hours. The CaO was then hydrated by exposure to an atmosphere of saturated water vapor at 23° for two months. The containers were lined with ceresin. The specific surface area of the calcium hydroxide was determined by the B.E.T. method,[10] using nitrogen adsorption; it was found to be 36.8 m.^{2}/g.

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[6] S. Brunauer, J. C. Hayes and W. E. Hass, This Journal, **58**, 279 (1954).

[7] Ernest M. Grunwald, unpublished Portland Cement Association reports; Chem. Dept., Florida State University, Tallahassee, Florida.

[8] L. E. Copeland and J. C. Hayes, ASTM Bulletin, No. 194, December, 1953.

[9] B. Franke, *Z. anorg. allgem. Chem.*, **247**, 180 (1941).

(b) Ca(OH)$_2$(II).—The same CaO was used, but it was hydrated in boiling water. The surface area of this sample was 5.8 m.^{2}/g.

Ignition loss and carbon dioxide determinations indicated complete hydration and very slight carbonation for both preparations.

Other Operations.—The ignition loss and carbon dioxide content were determined, the chemical analyses were performed, and the compositions of the substances were calculated according to the methods described by Brunauer, Hayes and Hass.[6]

Density determinations were made at 27° by the liquid-displacement method. The liquid used was a saturated solution of calcium hydroxide in water.

Dr. Greenberg of the Johns–Manville Research Center examined several of our samples by the methods[11] of differential thermal analysis and Chevenard thermobalance measurements.

X-Ray Investigations.—Cu Kα radiation was used in all cases. X-Ray diffraction patterns were obtained with a 114.6 mm. diameter Debye–Sherrer camera, a Norelco Wide Range Geiger Counter Diffractometer, or with a Norelco Counting Rate Computer used in conjunction with the diffractometer. This combination performs "fixed count" scanning automatically.

Specimens were protected from carbon dioxide and water vapor during use of the diffractometer by a simple modification of the scatter shield of the instrument. A thin sheet of polyethylene was sealed over the X-ray beam opening of the scatter shield, thereby providing a sealed chamber for the specimen during normal operation, with negligible loss of intensity. A test in which a sample of Ca(OH)$_2$(I) was held for 24 hours in the sealed enclosure showed no measurable change in carbon dioxide content, and a barely perceptible increase in ignition loss.

Except for the materials which were already sufficiently fine-grained, all samples were ground to pass a 200-mesh sieve and then further ground by hand for about 30 minutes in a mullite mortar. This procedure ensures good mixing of the constituents of the prepared mixtures, and it produces the fine-grained material necessary for reproducible intensity measurements.[12] The grinding was carried out in the controlled-atmosphere cabinet.

The most troublesome aspect of X-ray quantitative analysis, particularly of mixtures containing platy or fibrous materials, is preferred orientation. A modification of the technique described by Swanson and Tatge[13] enabled us to produce specimens for the diffractometer remarkably free from preferred orientation. Details of the specimen-preparation technique will be published later by Copeland and Bragg.

All quantitative analyses were performed with the diffractometer. Intensity data were obtained either by means of rate-meter recording, with the goniometer scanning at $^1/_8$° 2θ/minute, or by means of automatic "fixed count" scanning with the computer set for angular increments of 0.05°2θ. Corrections for Geiger counter lost

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(10) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

(11) S. A. Greenberg, This Journal, **58**, 362 (1954).

(12) L. Alexander, H. P. King and E. Kummer, *J. Appl. Phys.* **19**, 742 (1948).

(13) H. E. Swanson and E. Tatge, *J. Research Natl. Bur. Standards* **46**, 318 (1951).

counts were found to be unnecessary. The number of counts was such that the instrumental error in intensity measurements was usually less than 1%.

Results and Discussion

The stoichiometry of the hydration of Ca_3SiO_5 at 23° in a saturated calcium hydroxide solution can be represented by the equation

$$2Ca_3SiO_5 + 6H_2O = Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

The formula, $Ca_3Si_2O_7 \cdot 3H_2O$, is not intended to imply here anything about the structure of the calcium silicate hydrate. The water may be present in the hydroxylic form or as molecular water in the compound. Both ball-mill hydration and paste hydration can be *formally* represented by the same equation, but the calcium silicate hydrates are different. In ball-mill hydration the hydrate produced *is* afwillite; in paste hydration the product obtained *is similar to* tobermorite. To distinguish between the two calcium silicate hydrates, we shall adopt the notation $Ca_3Si_2O_7 \cdot 3H_2O$ (A) for afwillite and $Ca_3Si_2O_7 \cdot 3H_2O$ (T) for the tobermorite-like hydrate.

The Water of Hydration.—Jacquemin[14] hydrated Ca_3SiO_5 in a ball mill, and he concluded that the water of hydration was 3 molecules per molecule. Grunwald,[7] who investigated ball-mill hydration at our laboratory a few years ago, arrived at the same conclusion.

We hydrated several batches of Ca_3SiO_5 in the ball mill and obtained complete hydration in about 6 days, as will be shown later. The water of hydration corresponded almost exactly to 3 molecules of water per molecule of Ca_3SiO_5. We may mention two examples of this. The total water of hydration of one batch of hydrated Ca_3SiO_5(I), calculated on the assumption that Ca_3SiO_5 takes up 3 and Ca_2SiO_4 2 molecules of water, was 23.21% on ignited-weight basis. The experimental value was 23.11%. The total calculated water of hydration of another batch of hydrated Ca_3SiO_5(I) was 23.25%; the experimental value was 23.16%.

It is somewhat surprising to obtain such close agreement between theoretical and experimental values in a colloidal system. Afwillite, the calcium silicate hydrate produced in the ball-mill hydration of Ca_3SiO_5, is obtained in the form of particles having an average dimension of less than 300 Å. Nevertheless, afwillite even in this size range is stable at a water vapor pressure of 5×10^{-4} mm., indicating that its dissociation pressure at 23° has a lower value than that.

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[14] R. Jacquemin, "Recherches sur l'hydration des liants hydrauliques," Dissertation, University of Liege, Desoer, Liege, 1944.

The Reaction Products.—There was no evidence of unhydrated Ca_3SiO_5 on any of our X-ray diffractometer charts after 6 days of ball-mill hydration. All lines on the charts were attributable to calcium hydroxide and the calcium silicate hydrate.

The amount of $Ca(OH)_2$ in the products was first determined by the modified Franke method, described earlier. The result corresponded almost exactly to 1.5 molecules of $Ca(OH)_2$ per molecule of Ca_3SiO_5. Three examples are given below.

1. Batch I of hydrated Ca_3SiO_5(I) contained a total calculated value of 35.79% uncombined CaO. We assumed that the hydration of Ca_3SiO_5 produced 1.5 molecules of $Ca(OH)_2$ per molecule, and the hydration of Ca_2SiO_4 0.5 molecule of $Ca(OH)_2$ per molecule. The experimental result was 35.76% uncombined CaO.
2. Batch II of hydrated Ca_3SiO_5(I) had a calculated uncombined CaO content of 35.30%. The experimental value was 35.42%.
3. The above analyses were performed by hot extractions. Cold extraction of batch II of hydrated Ca_3SiO_5(I) gave an experimental value of 35.33%.

In spite of the extraordinary agreement between the calculated and experimental values, chemical analysis did not settle the stoichiometry of the hydration of Ca_3SiO_5. It did not seem impossible, or even unlikely, that the extraction process had altered the hydration products. For example, it seemed possible, especially on the basis of prior information,[2] that the hydration proceeded according to the reaction

$$Ca_3SiO_5 + 3H_2O = Ca_2SiO_4 \cdot 2H_2O + Ca(OH)_2 \quad (2)$$

and that during extraction the higher-lime hydrate decomposed

$$2(Ca_2SiO_4 \cdot 2H_2O) = Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2 \quad (3)$$

X-Ray investigation of the hydration products before and after extraction settled the question definitely. Diffractometer charts of the hydration products established the fact that in both cases the calcium silicate hydrate was afwillite, $Ca_3Si_2O_7 \cdot 3H_2O$ (A). Other than the calcium hydroxide lines only the lines of afwillite were present, with one possible exception. On some charts there was a vague indication of the strongest line of the tobermorite-like hydrate, $Ca_3Si_2O_7 \cdot 3H_2O$ (T), the one at 3.03 Å. Although a quantitative estimation could not be made, probably less than 5% of the calcium silicate hydrate was tobermorite.

The material from which the calcium hydroxide had been extracted showed complete absence of the calcium hydroxide lines on the charts; only afwillite lines were present. This was true of both the hot-extracted [Afwillite (H)] and the cold-extracted [Afwillite (C)] material. We mixed Afwillite (C) with $Ca(OH)_2$ in the proportion of three moles of $Ca(OH)_2$ to one mole of afwillite. Two mixtures were prepared: mixture A [Afwillite (C) plus $Ca(OH)_2$I] and mixture B [Afwillite (C) plus $Ca(OH)_2$-II].

X-Ray diffractometer charts of the two mixtures were prepared, and they were compared with charts of completely hydrated, unextracted Ca_3SiO_5 (Hydrated Ca_3SiO_5). The comparisons were based on the intensities of the four strongest lines of afwillite and the two strongest lines of calcium hydroxide. The line intensities obtained on seven charts are given in Table I.

TABLE I

LINE INTENSITY MEASUREMENTS

	$Ca(OH)_2$ lines		Afwillite lines			
	4.90 Å.	2.63 Å.	6.61 Å.	3.18 Å.	2.83 Å.	2.73 Å.
Alfwillite (H)			269	457	680	423
Afwillite (C)			246	424	604	391
Hydrated		981		311	473	293
Ca_3SiO_5	718	914	168	291	435	267
Mixture A	547	986	137	260	377	243
Mixture B		885			488	288
Mixture B	501	823	157	264	392	248

The intensities are given in arbitrary units (actually the number of squares on our charts). To ascertain whether the relative amounts of calcium hydroxide and afwillite were the same in hydrated Ca_3SiO_5 and in the two mixtures, we calculated the ratios of the intensities of each of the afwillite lines to each of the calcium hydroxide lines for each chart and compared the ratios obtained for hydrated Ca_3SiO_5 with the ratios obtained for the mixtures. The intensities shown in Table I enabled us to make 26 such comparisons. The result was that the afwillite content of hydrated Ca_3SiO_5 was 98.7% of the afwillite content of mixture A or B (or, what is the same thing, the calcium hydroxide content of hydrated Ca_3SiO_5 was 101.3% of the calcium hydroxide content of mixture A or B). The standard error of the mean was 3.4%. It will be noted that in the comparison we used *relative* intensities, the calcium hydroxide serving as an internal standard or the afwillite and *vice versa*.[15]

We can definitely conclude from these data that

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(15) L. Alexander and H. P. Klug, *Anal. Chem.*, **20**, 886 (1948).

the stoichiometry of the hydration of Ca_3SiO_5 in the ball mill at 23° in saturated calcium hydroxide solution is represented by the equation

$$2Ca_3SiO_5 + 6H_2O = Ca_2Si_2O_7 \cdot 3H_2O(A) + 3Ca(OH)_2 \quad (4)$$

Calcium Hydroxide.—The calcium hydroxide produced in the hydration of Ca_3SiO_5 appeared in the form of crystals having larger than colloidal dimensions. The calcium hydroxide in mixture A had a surface area of 36.8 $m.^2/g.$; that in mixture B a surface area of 5.8 $m.^2/g.$ Comparison of the half-intensity widths of the calcium hydroxide lines obtained for these mixtures with those of the calcium hydroxide lines obtained for hydrated Ca_3SiO_5 indicated that the dimensions of the calcium hydroxide crystallites in the latter were intermediate between the dimensions of the crystallites in the two mixtures and closer to the dimensions of the low-surface calcium hydroxide. The line widths also clearly indicated that the crystallites of calcium hydroxide were stubby. Surface–area determinations by water–vapor adsorption indicated about the same average particle dimension as X-ray line broadening did.

Afwillite.—The d spacings of the X-ray diffraction lines of the afwillite produced in the ball-mill hydration of Ca_3SiO_5 showed a very close correspondence to the d spacings published by various investigators for the natural mineral afwillite, especially to those published by Switzer and Bailey.[16] Interestingly, however, the relative intensities of our lines did not show such a close correspondence to published values. A comparison between our results and those of others for the four strongest lines of afwillite is given in Table II.

The discrepancy between our results and those of others is explainable on the basis of preferred orientation in the samples of other investigators. Our artificial afwillite was obtained in colloidal dimensions, after six days of grinding; we believe, therefore, that the particles had random orientation. This is evidenced also by the close agreement between the relative intensities obtained on seven charts, shown in Table II.

We received from the U. S. National Museum a sample of natural afwillite, which came from the Dutoitspan mine, Kimberly, South Africa. Debye–Sherrer patterns made on parts of the sample showed that (a) the 2.83 Å. line was the strongest line; (b) the 3.18 and 2.73 Å. lines had about the same inten-

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(16) G. Switzer and E. H. Bailey, *Am. Mineralogist*, **38**, 629 (1953).

(17) Imperial Chemical Industries, Norwich.

(18) H. F. McMurdie and E. P. Flint, *J. Research Natl. Bur. Standards*, **31**, 227 (1943).

TABLE II

RELATIVE INTENSITIES OF AFWILLITE LINES

	Afwillite lines			
	6.61 Å.	3.18 Å.	2.83 Å.	2.73 Å.
A. Our Values				
Afwillite (H)	40	67	100	62
Afwillite (C)	41	70	100	65
Hydrated Ca_3SiO_5	..	66	100	62
Hydrated Ca_3SiO_5	39	67	100	61
Mixture A	36	69	100	64
Mixture B	..	..	100	59
Mixture B	40	67	100	63
Av.	40	67	100	62
B. Values of Others				
Switzer and Bailey[16]	90	90	100	90
Imperial Chemical Industries, Ltd.[17]	70	90	100	90
McMurdie and Flint[18]	80	100	100	80
Av. of others' values	80	93	100	87

sities, and their intensities were about two-thirds of the intensity of the 2.83 Å. line; and (c) the intensity of the line at 6.61 Å. had about one-half the intensity of the 2.83 Å. line. The Debye–Sherrer patterns of our artificial afwillite were indistinguishable from those of natural afwillite.

We prepared six X-ray diffractometer charts of natural afwillite and calculated the relative intensities. The results are shown in Table III.

A comparison of Table III with Table II shows that the relative intensities of the four strongest lines of natural and artificial afwillite are in very good agreement. On the basis of these results we conclude that there is no difference, detectable by the X-ray techniques employed by us, between the

TABLE III

RELATIVE INTENSITIES OF NATURAL AFWILLITE LINES

Chart no.	Afwillite lines			
	6.61 Å.	3.18 Å.	2.83 Å.	2.73 Å.
1	48.2	59.9	100	69.0
2	57.3	61.7	100	78.7
3	41.1	60.3	100	79.1
4	46.1	67.9	100	56.5
5	47.0	77.4	100	79.3
6	41.3	63.5	100	51.6
Av.	46.8	65.1	100	69.0
Standard error of mean, %	2.4	2.7	..	5.0

natural mineral afwillite and the artificial afwillite obtained in the ball-mill hydration of Ca_3SiO_5.

Megaw[19] recently determined the crystal structure of afwillite and showed that the formula $Ca_3(SiO_3OH)_2 \cdot 2H_2O$ best represented its structure. From the structure data she calculated the density of afwillite to be 2.643 ± 0.005 g./cc. She used natural afwillite from the Dutoitspan mine for the structure determination. We determined the density of our afwillite, obtained from ball-mill-hydrated Ca_3SiO_5 by hot-extraction of calcium hydroxide. The experimental density was 2.642 ±0.01 g./cc., the density corrected for impurities (on additive basis) was 2.647 ± 0.01 g./cc.

For the indices of refraction of afwillite from Crestmore, California, Switzer and Bailey[16] reported the values $\alpha = 1.616$, $\beta = 1.619$, $\gamma = 1.631$. The average index of refraction of our sample of Dutoitspan afwillite was 1.62 ± 0.01. The average index of refraction of our artificial colloidal afwillite was also 1.62 ± 0.01.

The specific surface area of afwillite obtained from the ball-mill hydration of Ca_3SiO_5 was found to be 84 ± 4 m.^{2}/g. by the B.E.T. method.[10] It was determined both by nitrogen adsorption at the boiling point of nitrogen and by water vapor adsorption at 25°. Using the customary value of 16.2 Å.^{2} for the molecular area of nitrogen, we obtain identical surface area with water vapor, if we assume that the latter had a molecular area of 11.8 Å.^{2}; a reasonable molecular area.

If the afwillite particles were spherical and all the same size, the surface area would indicate a particle diameter of about 285 Å. Electron micrographs, obtained by Swerdlow, McMurdie and Heckman[20] from our artificial afwillite showed that the particles were roughly spherical and had dimensions of the order of 250 Å.

Differential thermal analysis results were reported by Moody[21] for natural afwillite from Kimberly. She stated that the chart "shows an endothermic reaction proceeding in several steps in the temperature range 250–450°, the most marked reaction occurring at approximately 370°, and an exothermic reaction which takes place at about 820°. It seems clear that these correspond to the dehydration process and to the formation of rankinite, respectively."

The main features of the differential thermal anal-

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(19) H. D. Megaw, *Acta Cryst.*, **5**, 477 (1952).

(20) M. Swerdlow, H. F. McMurdie and F. A. Heckman, "Proc. of the International Conference on Electron Microscopy," London, 1954; *J. Roy. Micro. Soc.* (in press).

(21) K. M. Moody, *Mineral. Mag.*, **29**, 838 (1952).

ysis curve of our artificial afwillite were the same as those of natural afwillite. There were endothermic minima at 240, 320 and 470°, which, doubtless, correspond to the steps reported by Moody for the temperature range 250–450°. The slight shifts in temperature are not significant; they may be caused by differences in techniques. The minima at 240 and 320° probably correspond to the loss of the two types of water in afwillite, $Ca_3(SiO_3OH)_2 \cdot 2H_2O$. The most marked reaction occurs at 320°. There is a strong exothermic peak at 820°, which may possibly be due to the formation of wollastonite, β-$CaSiO_3$, rather than rankinite, $Ca_3Si_2O_7$. In addition to the peaks reported by Moody, Greenberg obtained an endothermic peak at 125°, which may be due to the loss of adsorbed water. The absence of the peak in natural afwillite may be explained on the basis of difference in surface area; our artificial afwillite had colloidal dimensions, whereas the specific surface area of natural afwillite was negligible compared with that of our artificial afwillite.

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THE STOICHIOMETRY OF THE HYDRATION OF TRICALCIUM SILICATE AT ROOM TEMPERATURE. II. HYDRATION IN PASTE FORM

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Evidence is presented that the stoichiometry of the hydration of tricalcium silicate, Ca_3SiO_5, in the form of hardened paste in a saturated calcium hydroxide solution at 23° may be represented by the equation $2Ca_3SiO_5 + 6H_2O = Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2$. An initial H_2O/Ca_3SiO_5 weight ratio of 0.7 was used, and the pastes were hydrated for 2 to 2.5 years. X-Ray and microscopic examinations indicated almost complete hydration. The calcium silicate hydrate produced was similar to the natural mineral tobermorite; its density was 2.44 ± 0.01 g./cc., and its average index of refraction was 1.56 ± 0.015. Bernal proposed the structural formula $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$ for the hydrate. The artificial tobermorite was colloidal in dimensions; nitrogen adsorption, X-ray line broadening and electron micrographs indicated on average dimension of about 100 Å. About 15% of the calcium hydroxide was adsorbed on the tobermorite surface; the rest of the calcium hydroxide appeared in the form of relatively large crystals, visible under the microscope.

Introduction

The stoichiometry of the hydration of tricalcium silicate, Ca_3SiO_5, in a steel ball mill in a saturated calcium hydroxide solution at 23° was discussed in the previous paper.[1] The present paper discusses the stoichiometry of the hydration of Ca_3SiO_5 in the form of "paste." The term "paste" as used by cement chemists, and as used here, means a plastic or semi-fluid mixture of a hydraulic material, such as portland cement, Ca_3SiO_5 or Ca_2SiO_4, with water. After a few hours the paste "sets" and then hardens; the present investigations were carried out on hardened pastes.

Experimental

The experimental techniques employed were in most respects identical with those described before.[1] Only a few additional remarks are needed here.

Pastes of Ca_3SiO_5 were prepared by the method described by Brunauer, Hayes and Hass,[2] except that the pastes were cast as solid cylinders, without a hole in the center. The water-to-Ca_3SiO_5 weight ratio was 0.7. The pastes prepared from Ca_3SiO_5(I) were hydrated for 21 months; those prepared from Ca_3SiO_5(II) were hydrated for 30 months. The hydration was conducted in a room kept at 23 ± 0.5°.

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[1] S. Brunauer, L. E. Copeland and R. H. Bragg, This Journal, **60**, 112 (1956).

[2] S. Brunauer, J. C. Hayes and W. E. Hass, *ibid.*, **58**, 279 (1954).

The uncombined water was removed by the method described by Brunauer, Hayes and Hass.[2]

The calcium hydroxide, $Ca(OH)_2$(III), used in the present experiments was different from those described before.[1] Calcium oxide was prepared from "Baker analyzed" reagent grade $CaCO_3$, low in alkalies, by ignition at 900 to 950° for 16 hours. The hydration was carried out in a polyethylene bottle, by letting the CaO stand in water at 25° for three months and shaking the bottle once or twice a day.

Results and Discussion

X-Ray diffractometer charts of the hydrated Ca_3SiO_5 pastes showed the presence of calcium hydroxide and tobermorite lines only. The calcium silicate hydrates, designated as tobermorites, vary in molar CaO/SiO_2 ratio from 1.0 (or 0.8) to 1.5. In a saturated calcium hydroxide solution the compound with the highest lime-to-silica ratio is obtained.[1] This compound has the formula $Ca_3Si_2O_7 \cdot 3H_2O$ according to Bernal,[3] and the formula $Ca_3Si_2O_7 \cdot 2H_2O$ according to Taylor.[4] The formulas, as written here, are not intended to imply anything about the structures of the molecules; water may be present in the structure either in the molecular or in the hydroxylic form, or in both forms.

The stoichiometry of the hydration of Ca_3SiO_5 may be represented by the equation

$$2Ca_3SiO_5 + 6H_2O = Ca_3Si_2O_7 \cdot 3H_2O(T) + 3Ca(OH)_2 \quad (1)$$

if Bernal's formula is correct, or by the equation

$$2Ca_3SiO_5 + 5H_2O = Ca_3Si_2O_7 \cdot 2H_2O + 3Ca(OH)_2 \quad (2)$$

if Taylor's formula is right. (The (T) after $Ca_3Si_2O_7 \cdot 3H_2O$ is added to distinguish this compound from afwillite.[1]) It will be shown that the weight of evidence favors eq. 1. Other reactions than those represented by eq. 1 and 2 will be considered in the last section of the paper.

The Water of Hydration.—The water of hydration was determined by the same method that was employed for the ball-mill hydration products.[1] If we call the stoichiometric water of hydration, according to eq. 1, 100%, then two pastes prepared from Ca_3SiO_5(I) contained 86.0 and 83.7, and one paste prepared from Ca_3SiO_5(II) contained 84.5% of the stoichiometric quantity of water. These numbers represent *minimum* values. Both Ca_3SiO_5 preparations contained approximately 96% Ca_3SiO_5, 3% β-Ca_2SiO_4 and 1% of other impurities. The values for the water of hydration were calculated on the assumptions that (1) the hydratable

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(3) J. D. Bernal, "Proceedings of the Third International Symposium on the Chemistry of Cement," London, 1952, p. 216.

(4) H. F. W. Taylor, *J. Chem. Soc.*, 163 (1953).

impurities (tricalcium aluminate, calcium oxide and magnesium oxide) were fully hydrated; and (2) the fraction of β-Ca_2SiO_4 hydrated was the same as the fraction of Ca_3SiO_5 hydrated.

Pure β-Ca_2SiO_4 hydrates at a much slower rate than Ca_3SiO_5. A hardened paste of β-Ca_2SiO_4, which had hydrated for about the same period as the three Ca_3SiO_5 pastes, contained only 37.5% of the stoichiometric amount of water of hydration (2 molecules of water per molecule of Ca_2SiO_4).[2] If we assume that the Ca_2SiO_4 in the Ca_3SiO_5 paste hydrated at the same rate as in its own paste, then the Ca_3SiO_5 in the three pastes contained 87.3, 85.0 and 85.3% of the stoichiometric quantity of water according to eq. 1. These are not necessarily *maximum* values, since in this calculation we have assumed again that all hydratable impurities, with the exception of Ca_2SiO_4, were fully hydrated. The water of hydration of Ca_3SiO_5 in the three pastes was probably between the two sets of values given above.

Equation 2 implies that the water of hydration is only $^5/_6$ of that indicated by eq. 1, or 83.3%. Our values were between 83.7 and 87.3%. Two arguments may be advanced against eq. 2.

1. The first may be adduced from consideration of the sizes of the tobermorite particles. We shall show later that the average particle dimension is of the order of 100 Å. which approaches the lower size range even in colloidal systems. The dissociation pressure of the calcium silicate hydrate in this size range should be greater than that of normal crystals; the water content of the hydrate at a vapor pressure of 5×10^{-4} mm. should, therefore, be *at most* equal to and probably smaller than the stoichiometric water content in a saturated calcium hydroxide solution. This could explain why the water contents of the pastes were smaller than the quantities indicated by eq. 1, but all our water values were greater than that corresponding to eq. 2.

2. A second and perhaps more decisive argument against eq. 2 may be cited from crystal structure considerations. It was shown by Taylor[5] that his calcium silicate hydrate (I), or artificial tobermorite, was a layer crystal and that the structure of the layers did not change with increasing CaO/SiO_2 ratio. A hydrate with a molar CaO/SiO_2 ratio of 0.92 gave the same X-ray diffraction line pattern as a hydrate with a CaO/SiO_2 ratio of 1.41. This can be explained by assuming that the lime in excess of 1 mole per mole of SiO_2 was located between the layers, as was postulated by Bernal.[3] In this

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(5) H. F. W. Taylor, *ibid.*, 3682 (1950).

case, however, it is difficult to imagine the existence of unhydrated or incompletely hydrated CaO in an aqueous system between layers of hydrated calcium silicate. Bernal assumed layers of $Ca(OH)_2$ between the calcium silicate hydrate layers, which seems more reasonable, and which would lead to the stoichiometry represented by eq. 1.

Taylor arrived at the formula $Ca_3Si_2O_7 \cdot 2H_2O$ on the basis of dehydration experiments.[4] We conducted some dehydration experiments, which will be published in more detail in the future by Brunauer, Kantro and Weise. Tobermorites having CaO/SiO_2 ratios of 1.0 and 1.5 were prepared by the reaction of calcium hydroxide and hydrous silica at 23°. In the course of drying at a water vapor pressure of 5×10^{-4} mm., both hydrates lost approximately one-third of their water of hydration, one retaining only 0.65 mole of water, the other about 1 mole of water per mole of SiO_2. The tobermorite obtained in the paste hydration of Ca_3SiO_5 also lost roughly one-third of its water of hydration under the same drying conditions. On the other hand, when a less drastic drying agent was used, more of the water of hydration was retained. At a vapor pressure of 8×10^{-3} mm., produced by a mixture of magnesium perchlorate dihydrate and tetrahydrate, about 14% more water was retained by hydrated Ca_3SiO_5 pastes than at 5×10^{-4} mm. pressure.

On the basis of the above considerations, we conclude that eq. 2 does not represent the stoichiometry of the paste hydration of Ca_3SiO_5 in a saturated calcium hydroxide solution at room temperature.

Calcium Hydroxide.—We were unable to determine the calcium hydroxide content of paste-hydrated Ca_3SiO_5 by chemical means because the solvents used both in the Franke method[6] and the Lerch and Bogue method[7] removed some of the lime from the high-lime tobermorite.

The calcium hydroxide content of the hydrated paste was determined by X-ray line intensity measurements. The paste used in these determinations was prepared from Ca_3SiO_5(II). The lime was extracted from a portion of the paste by a modification of the Franke method,[1] and a known quantity of calcium hydroxide (III) was added to the remaining tobermorite (mixture C). Comparison of the intensities of the two strongest calcium hydroxide lines obtained from the Ca_3SiO_5 paste and from mixture C gave the weight fraction of $Ca(OH)_2$ in the former.

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[6] B. Franke, *Z. anorg. allgem. Chem.*, **247**, 180 (1941).

[7] W. Lerch and R. H. Bogue, *Ind. Eng. Chem.*, *Anal. Ed.*, **2**, 296 (1930).

We prepared X-ray diffractometer charts of six samples of the Ca_3SiO_5 paste, and six of mixture C. The results are shown in Table I.

TABLE I

INTENSITIES OF CALCIUM HYDROXIDE LINES

Chart No.	Mixture C		Chart No.	Ca_3SiO_5 Paste	
	$Ca(OH)_2$ lines			$Ca(OH)_2$ lines	
	4.90 Å.	2.63 Å.		4.90 Å.	2.63 Å.
1	557	848	1A	616	747
2	565	839	2A	411	748
3	..	847	3A	..	718
Av.	561	845		513	738
4	576	878	4A	411	788
5	644	876	5A	598	871
6	..	888	6A	..	777
Av.	610	881		505	812

Charts 1, 2, 3 and 1A, 2A, 3A were obtained on the same day, and the average intensity of each calcium hydroxide line obtained for one of the materials was compared with the average intensity of the same line obtained for the other material. Likewise, charts 4, 5, 6 and 4A, 5A, 6A were obtained on the same day, and the average intensities were compared in a similar manner. Such precautions are important because it is difficult to reproduce the voltage and current settings exactly from day to day. Mixture C contained 38.8% calcium hydroxide; the uncorrected percentage of calcium hydroxide in the Ca_3SiO_5 paste based on the intensities given in Table I was 34.1 ± 0.3%. Correction for the differences in mass absorption coefficients lowered this value to 33.9 ± 0.3%. (This result has since been confirmed using an internal standard, to be published by Copeland and Bragg.)

Dr. S. A. Greenberg of the Johns-Manville Research Center determined the calcium hydroxide content of our Ca_3SiO_5 paste by his Chevenard thermobalance and obtained a value of 34.7%. This is in good agreement with our X-ray value of 33.9%. The latter value corresponds to 85.4 ± 0.8% of the stoichiometric amount according to eq. 1. The missing 15% of calcium hydroxide may be ascribed to adsorption on the tobermorite surface. As will be seen later, the specific surface area of tobermorite is large; it can account for the adsorption of this amount of calcium hydroxide without difficulty. The adsorbed calcium hydroxide decomposes at lower temperatures than crystalline calcium hydroxide and, because of the heterogeneity of the surface, over a range of temperatures.

This is the reason why the thermobalance results, giving the values for crystalline calcium hydroxide, checked the X-ray results so well.

In contrast with the finely divided tobermorite, the calcium hydroxide produced in the paste-hydration of Ca_3SiO_5 appeared in the form of relatively large crystals, easily visible under the microscope. The X-ray diffraction lines were sharp, indicating larger calcium hydroxide crystals than those produced in the ball-mill hydration of Ca_3SiO_5.[1]

The Extent of Hydration of Ca_3SiO_5.—The Ca_3SiO_5 paste, discussed in the previous section, contained 85.4 ± 0.8% of the stoichiometric amount of calcium hydroxide according to eq. 1. Earlier we discussed the two ways of calculating the water of hydration of Ca_3SiO_5 pastes. The values for this particular paste were 84.5 and 85.3%; the average was 84.9 ± 0.4% of the stoichiometric water of hydration according to eq. 1. Because these independent determinations showed such excellent agreement, we believed at first that the Ca_3SiO_5 paste was only 85% hydrated in 2.5 years. However, this did not turn out to be the case.

We were unable to detect more than a very small amount of unhydrated Ca_3SiO_5 in the above paste by means of our X-ray diffractometer. We determined the amount of unhydrated Ca_3SiO_5 in the paste by diluting samples of the paste with known quantities of Ca_3SiO_5 and comparing the mixtures with the undiluted paste. The result was 0.5% unhydrated Ca_3SiO_5 in the paste. Details of the method will be presented later by Copeland and Bragg.

Microscopic examination of the Ca_3SiO_5 paste confirmed the X-ray results; it indicated less than 1% unhydrated Ca_3SiO_5. We had to conclude, therefore, that the Ca_3SiO_5 paste was almost completely hydrated. As stated in the two previous sections, the deficiency in the water of hydration may be ascribed to partial decomposition of the tobermorite under our drying conditions, and the deficiency in calcium hydroxide to adsorption on the tobermorite surface. The fact that the deficiency was 15% in both cases is probably sheer coincidence; for the time being we have no other explanation for it.

Tobermorite.—1. On the basis of crystal structure and other considerations, Bernal[3] suggested that the tobermorite system of hydrates might be represented by the structural formula

$$Ca[SiO_2(OH)_2][Ca(OH)_2]_x[H_2O]_y$$

where x varies from 0 to 0.5 and y from 0 to 1.0.

We shall disregard the $[H_2O]_y$ term, which represents adsorbed or zeolitic water. We cannot tell how much adsorbed water is attached to the surface of the hydrate in the saturated calcium hydroxide solution, and the hydrate dried under our drying conditions contains little or no adsorbed water.

The low-lime end-member of the tobermorite series would be the compound $Ca[SiO_2(OH)_2]$, in which two of the oxygen ions of the SiO_4 tetrahedron are replaced by hydroxyl ions. The compounds containing more lime, according to Bernal, "would represent an addition of epi-axially arranged $Ca(OH)_2$ layers, possibly on both sides of the calcium silicate layers. The spacings of the two are sufficiently alike to permit this."

Much has been written by different investigators on the question whether the lime in excess of a CaO/SiO_2 ratio of 1.0 is adsorbed or whether it is in solid solution. Steinour[8] pointed out that a zeolitic solid solution, the type that exists in the tobermorites, can be regarded as "a special kind of internal adsorptive system"; it does not make any difference, therefore, whether we call it one or the other. We share Steinour's point of view, and we add that if we call the zeolitic uptake of lime adsorption, it should be clear that it is *chemical adsorption*. The fact that the high-lime end-member of the tobermorite series has a definite composition clearly indicates that the phenomenon is not physical adsorption. If the extra lime were physically adsorbed on the monocalcium silicate hydrate, the uptake of lime would be a function of the specific surface area of the hydrate, and we would find that the CaO/SiO_2 ratio of the high-lime end-member of the series would vary with the specific surface area. However, there is no such variation. Greenberg[9] determined the CaO/SiO_2 ratio of the high-lime end-member of the series and obtained a value of 1.5 within his experimental error. He also measured the surface areas of some of his preparations by nitrogen adsorption, and the *largest* specific surface area he obtained was only about one-third as large as that of our tobermorite.

The tobermorite we obtained in the paste-hydration of Ca_3SiO_5 in a saturated calcium hydroxide solution at 23° was the high-lime end-member of the tobermorite series, having a CaO/SiO_2 ratio of 1.5. Bernal's structural formula for this compound may be written as $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$. Since we found nothing in our experiments that would contradict this formula, we tentatively

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(8) H. H. Steinour, *Chem. Revs.*, **40**, 391 (1947).

(9) S. A. Greenberg, THIS JOURNAL, **58**, 362 (1954).

accept it as the structural formula of our tobermorite.

2. Whereas the X-ray diffraction line pattern of artificial afwillite, produced in the ball-mill hydration of Ca_3SiO_5, was identical with that of the natural mineral afwillite,[1] the line pattern of our artificial tobermorite was far from being identical with that of the natural mineral tobermorite. Claringbull and Hey[10] listed 29 lines for the natural mineral from Tobermory pier and 32 lines for one of Taylor's artificial tobermorites; but our tobermorite showed only four lines on the diffractometer charts. These four lines, a very strong and very broad line with the peak at about 3.03 Å., and three much weaker lines with peaks at about 11, 2.82 and 1.82 Å., correspond to the four strongest lines of Taylor's artificial tobermorite, obtained from the hydration of Ca_3SiO_5.[5] The scarcity of lines indicates poor crystallization; the widths of the lines indicate fine subdivision.

The fact that Taylor's tobermorite was much better crystallized than ours suggests that his crystals were also larger than ours. Greenberg's[9] tobermorite, like Taylor's, gave a large number of X-ray lines and, as we stated before, the surface area of his tobermorite was much smaller than that of ours. The smaller surface areas of Taylor's and Greenberg's crystals indicate a smaller adsorption of calcium hydroxide on the tobermorite surface, which would probably explain why the molar CaO/SiO_2 ratios of their hydrates were equal to 1.5 within their experimental errors.

Taylor[5] and Bernal[3] regard tobermorite as a layer crystal, with a variable distance between the layers, depending on the water content. Taylor obtained the value of 11 Å. for the distance between the calcium silicate hydrate layers, when the adsorbed (or zeolitic) water was removed. The X-ray diffractometer chart of our tobermorite showed a broad line with its peak at 11 Å. for the dry substance. On the other hand, Debye–Scherrer photographs, which were prepared by exposing the substance to laboratory air of about 40% relative humidity, showed a very broad line, extending from 11 to 15 Å. The broadening was, doubtless, caused by adsorbed water.

3. We determined the density of a Ca_3SiO_5 paste and obtained the value 2.406 ± 0.005 g./cc. The calculated density of the tobermorite in the paste, assuming additivity of the densities of the

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(10) G. F. Claringbull and M. H. Hey, *Mineral. Mag.*, **29**, 960 (1952).

constituents of the paste, was 2.44 ± 0.01 g./cc. We may compare this value with that of Taylor's artificial tobermorite. He did not measure the density, but it can be calculated from his crystal structure data. Heller and Taylor[11] found that their artificial tobermorite had an orthorhombic unit cell, with a = 5.62 Å., b = 3.66 Å., and c = 11.0 Å. Assuming that the cell contains one molecule of $Ca_3Si_2O_7 \cdot 3H_2O$, the density of the substance is 2.514 g./cc. A change in the c spacing from 11.0 to 11.3 Å. would give an exact agreement with our density value of 2.44 g./cc. Taylor found values for the c spacing ranging from 11.0 to 11.5 Å., and Greenberg[9] obtained the value of 11.3 Å. for artificial tobermorite. Claringbull and Hey[10] reported values ranging from 11.2 to 11.4 Å. for natural tobermorite. Our own value of 11 Å. may easily be in error to the extent of 0.3 Å. Thus, the density of our calcium silicate hydrate also indicates that it is artificial tobermorite.

4. Similar conclusion was reached from measurement of the index of refraction. It was found that the average index of refraction of our calcium silicate hydrate was approximately the same as that of calcium hydroxide, 1.56 ± 0.015. Claringbull and Hey[10] reported the value of 1.558 ± 0.003 for the mean index of refraction of natural tobermorite, and Heller and Taylor[12] obtained a mean refractive index of about 1.56 for artificial tobermorite.

5. The specific surface area of our artificial tobermorite was 220 m.^{2}/g. If we assume that the tobermorite particles were spherical and all the same size, the surface area leads to a particle diameter of 110 Å. We may compare this value with the average crystallite dimension, obtained from X-ray line broadening. Our tobermorite had only one strong line, with its peak at 3.03 Å. The half-intensity width of this line, corrected for instrumental broadening, gave an average crystallite dimension of 96 Å., which is in fair agreement with the nitrogen adsorption value. Electron micrographs, obtained by Swerdlow and Heckman,[13] likewise indicated particles of this order of magnitude.

Whereas the surface area values obtained for our artificial afwillite by nitrogen adsorption and by water vapor adsorption were the same, for our

(11) L. Heller and H. F. W. Taylor, *J. Chem. Soc.*, 2397 (1951).

(12) L. Heller and H. F. W. Taylor, *ibid.*, 2535 (1952).

(13) M. Swerdlow, H. F. McMurdie and F. A. Heckman, "Proceedings of the International Conference on Electron Microscopy," London, 1954. *J. Roy. Microsc. Soc.* (in press).

artificial tobermorite water vapor adsorption gave a larger surface than nitrogen adsorption. The surface available to water molecules was 320 m.^{2}/g. The discrepancy may be explained by assuming that water molecules can penetrate, to some extent, between the calcium silicate hydrate layers in tobermorite, whereas nitrogen molecules cannot. Afwillite is not a layer crystal, which would explain the agreement between water and nitrogen adsorption surface area values.

6. The differential thermal analysis curve of our Ca_3SiO_5 paste, obtained by Greenberg, showed only two peaks: one strong endothermic peak at 550°, which corresponds to the dehydration of calcium hydroxide, and one exothermic peak around 900°, which may correspond to the formation of wollastonite, or possibly rankinite. Thus, the DTA curves of afwillite[1] and tobermorite are very different.

The DTA curve of paste-hydrated Ca_3SiO_5 gave no indication of the presence of afwillite, nor did the X-ray diffractometer charts. On the other hand, tobermorite obtained from the Ca_3SiO_5 paste after the hot extraction of calcium hydroxide, showed unmistakably the presence of afwillite. The strongest afwillite line, the one at 2.83 Å., was not definitely identifiable, because it coincided with a tobermorite line, but the afwillite lines at 3.18 and 2.73 Å. were clearly identifiable. We may guess roughly that this tobermorite contained 10 to 20% afwillite.

The Stoichiometry of Paste Hydration.—The question may be raised whether other reactions than that represented by eq. 1 would explain our experimental results.

Bessey[14] and Taylor[5] found evidence of the existence of a dicalcium silicate hydrate in a saturated calcium hydroxide solution at 17°. If we assume that such a hydrate does form in the hydration of Ca_3SiO_5 at 23°, the stoichiometry of the reaction may be represented by the equation

$$Ca_3SiO_5 + xH_2O = Ca_2SiO_4\cdot(x-1)H_2O + Ca(OH)_2 \quad (3)$$

The quantity of lime produced in these reactions is 66.7% of that indicated by eq. 1. The quantity of lime we obtained was 85.4%; eq. 3, therefore, cannot represent the hydration reaction. If, however, we assume that in the hydration of Ca_3SiO_5 two calcium silicate hydrates are produced, $Ca_2SiO_4\cdot(x-1)H_2O$ and $Ca_3Si_2O_7\cdot3H_2O$(T), in the proportion of two molecules of the former to one of the latter, we can account approximately for our ex-

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(14) G. E. Bessey, "Proceedings of the Symposium on the Chemistry of Cements," Stockholm, 1938 p. 178.

perimental results. Nevertheless, we do not favor this explanation. Taylor's dicalcium silicate hydrate gave a pattern *very* similar to that of tobermorite. Our calcium silicate hydrate pattern resembled the latter more than the former. In addition, the DTA curves, the density and the average index of refraction indicated that the hydrate was tobermorite.

Another possible reaction that would give an approximate explanation for our results is

$$4Ca_3SiO_5 + 10H_2O = Ca_7Si_4O_{15} \cdot 5H_2O + 5Ca(OH)_2 \quad (4)$$

This reaction, at *complete* hydration, would indicate $^5/_6$ as much water of hydration and $^5/_6$ as much calcium hydroxide as eq. 1, which is not too far from the results we obtained. Nevertheless, we are reluctant to suggest this explanation. There are already two calcium silicate hydrates in the literature, having X-ray patterns practically indistinguishable from each other. It does not seem to us desirable to propose now the existence of a third hydrate, indistinguishable in X-ray pattern from tobermorite, and very similar to it in other properties.

All of our experimental results can be explained on the basis of the reaction represented by eq. 1, without the necessity of postulating new compounds or phenomena unfamiliar to the colloid chemist. Although the stoichiometry of the paste hydration of Ca_3SiO_5 is not as decisively settled as that of ball-mill hydration, the weight of evidence strongly favors the hydration reaction represented by eq. 1.

The lime is in two different forms in the calcium silicate hydrate; two-thirds of it is located in the calcium silicate hydrate layers, and one-third is in zeolitic solid solution or is adsorbed chemically. The calcium hydroxide is also in two different forms; under our experimental conditions 85% of it was in the crystalline form, and 15% was adsorbed on the tobermorite surface. Tobermorites, having smaller specific surface areas than ours, adsorb a smaller fraction of the calcium hydroxide. This appeared to be the case for the tobermorites of Taylor and Greenberg.

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Bulletins Published by the Research Department Research and Development Division of the Portland Cement Association

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Bulletin 16—"**Development and Study of Apparatus and Methods for the Determination of the Air Content of Fresh Concrete,**" by CARL A. MENZEL, May, 1947.

Reprinted from *Journal of the American Concrete Institute* (May, 1947); *Proceedings*, **43**, 1025 (1947).

Bulletin 17—"**The Problem of Proportioning Portland Cement Raw Mixtures: Part I—A General View of the Problem; Part II—Mathematical Study of the Problem; Part III—Application to Typical Processes; Part IV—Direct Control of Potential Composition,**" by L. A. DAHL, June, 1947.

Reprinted from *Rock Products*, **50**, No. 1, 109; No. 2, 107; No. 3, 92; No. 4, 122 (1947).

Bulletin 18—"**The System CaO-SiO_2-H_2O and the Hydration of the Calcium Silicates,**" by HAROLD H. STEINOUR, June, 1947.

Reprinted from *Chemical Reviews*, **40**, 391 (1947).

Bulletin 19—"**Procedures for Determining the Air Content of Freshly-Mixed Concrete by the Rolling and Pressure Methods,**" by CARL A. MENZEL, June, 1947.

Reprinted from *Proceedings, American Society for Testing Materials*, **47**, 833 (1947).

Bulletin 20—"**The Effect of Change in Moisture-Content on the Creep of Concrete under a Sustained Load,**" by GERALD PICKETT, July, 1947.

Reprinted from *Journal of the American Concrete Institute* (February, 1942); *Proceedings*, **38**, 333 (1942).

Bulletin 21—"**Effect of Gypsum Content and Other Factors on Shrinkage of Concrete Prisms,**" by GERALD PICKETT, October, 1947.

Reprinted from *Journal of the American Concrete Institute* (October, 1947); *Proceedings*, **44**, 149 (1948).

Bulletin 22—"**Studies of the Physical Properties of Hardened Portland Cement Paste,**" by T. C. POWERS and T. L. BROWNYARD, March, 1948.

Reprinted from *Journal of the American Concrete Institute* (October-December, 1946; January-April, 1947); *Proceedings*, **43**, 101, 249, 469, 549, 669, 845, 933 (1947).

Bulletin 23—"**Effect of Carbon Black and Black Iron Oxide on Air Content and Durability of Concrete,**" by THOMAS G. TAYLOR, May, 1948.

Reprinted from *Journal of the American Concrete Institute* (April, 1948); *Proceedings*, **44**, 613 (1948).

Bulletin 24—"**Effect of Entrained Air on Concretes Made with So-Called 'Sand-Gravel' Aggregates,**" by PAUL KLIEGER, November, 1948.

Reprinted from *Journal of the American Concrete Institute* (October, 1948); *Proceedings*, **45**, 149 (1949).

Bulletin 25—"**A Discussion of Cement Hydration in Relation to the Curing of Concrete,**" by T. C. POWERS, August, 1948.

Reprinted from *Proceedings of the Highway Research Board*, **27**, 178 (1947).

Bulletin 26—"**Long-Time Study of Cement Performance in Concrete.**" This bulletin comprises four installments of the report of this investigation, by F. R. McMillan, I. L. Tyler, W. C. Hansen, William Lerch, C. L. Ford, and L. S. Brown, August, 1948.

Reprinted from *Journal of the American Concrete Institute* (February-May, 1948); *Proceedings*, **44**, 441, 553, 743, 877 (1948).

Bulletin 27—"**Determination of the Air Content of Mortars by the Pressure Method,**" by Thomas G. Taylor, February, 1949.

Reprinted from *ASTM Bulletin*, No. **155**, 44 (December, 1948).

Bulletin 28—"**A Polarographic Method for the Direct Determination of Aluminum Oxide in Portland Cement,**" by C. L. Ford and Lorrayne Le Mar, April, 1949.

Reprinted from *ASTM Bulletin*, No. **157**, 66 (March, 1949).

Bulletin 29—"**The Nonevaporable Water Content of Hardened Portland-Cement Paste—Its Significance for Concrete Research and Its Methods of Determination,**" by T. C. Powers, June, 1949.

Reprinted from *ASTM Bulletin*, No. **158**, 68 (May, 1949).

Bulletin 30—"**Long-Time Study of Cement Performance in Concrete—Chapter 5. Concrete Exposed to Sulfate Soils,**" by F. R. McMillan, T. E. Stanton, I. L. Tyler, and W. C. Hansen, December, 1949.

Reprinted from a Special Publication of the American Concrete Institute (1949).

Bulletin 31—"**Studies of Some Methods of Avoiding the Expansion and Pattern Cracking Associated with the Alkali-Aggregate Reaction,**" by William Lerch, February, 1950.

Reprinted from *Special Technical Publication No. 99*, published by American Society for Testing Materials (1950).

Bulletin 32—"**Long-Time Study of Cement Performance in Concrete—Chapter 6. The Heats of Hydration of the Cements,**" by George J. Verbeck and Cecil W. Foster, October, 1949.

Reprinted from *Proceedings, American Society for Testing Materials*, **50**, 1235 (1950).

Bulletin 33—"**The Air Requirement of Frost-Resistant Concrete,**" by T. C. Powers; discussion by T. F. Willis.

Reprinted from *Proceedings of the Highway Research Board*, **29**, 184 (1949).

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Reprinted from *Journal of the American Concrete Institute* (October, 1950); *Proceedings*, **47**, 117 (1951).

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Reprinted from *Journal of the American Concrete Institute* (February, 1951); *Proceedings*, **47**, 433 (1951).

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Reprinted from *Proceedings of The Highway Research Board*, **30**, 187 (1951).

Bulletin 38—"**Long-Time Study of Cement Performance in Concrete—Chapter 7. New York Test Road,**" by F. H. Jackson and I. L. Tyler, October, 1951.

Reprinted from *Journal of the American Concrete Institute* (June, 1951); *Proceedings*, **47**, 773 (1951)

Bulletin 39—"**Changes in Characteristics of Portland Cement as Exhibited by Laboratory Tests Over the Period 1904 to 1950,**" H. F. Gonnerman and William Lerch.

Reprinted from *Special Publication No. 127* published by American Society for Testing Materals. (1952).

Bulletin 40—"**Studies of the Effect of Entrained Air on the Strength and Durability of Concretes Made with Various Maximum Sizes of Aggregate,**" by Paul Klieger.

Reprinted from *Proceedings of the Highway Research Board,* **31,** 177 (1952).

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Bulletin 42—"**An Investigation of Bond Anchorage and Related Factors in Reinforced Concrete Beams,**" by Carl A. Menzel and William M. Woods, November, 1952.

Bulletin 43—"**Ten Year Report on the Long-Time Study of Cement Performance in Concrete,**" by Advisory Committee of the Long-Time Study of Cement Performance in Concrete, R. F. Blanks, Chairman.

Reprinted from *Journal of the American Concrete Institute* (March, 1953); *Proceedings,* **49,** 601 (1953).

Bulletin 44—"**The Reactions and Thermochemistry of Cement Hydration at Ordinary Temperature,**" by Harold H. Steinour.

Reprinted from *Third International Symposium on the Chemistry of Cement,* London, September 1952.

Bulletin 45—"**Investigations of the Hydration Expansion Characteristics of Portland Cement,**" by H. F. Gonnerman, William Lerch, and Thomas M. Whiteside, June, 1953.

Bulletin 46—"**Theory of Volume Changes in Hardened Portland Cement Paste During Freezing,**" by T. C. Powers and R. A. Helmuth.

Reprinted from *Proceedings of the Highway Research Board,* **32,** 285 (1953).

Bulletin 47—"**The Determination of Non-Evaporable Water in Hardened Portland Cement Paste,**" by L. E. Copeland and John C. Hayes.

Reprinted from *ASTM Bulletin* No. **194,** 70 (December, 1953).

Bulletin 48—"**The Heats of Hydration of Tricalcium Silicate and beta-Dicalcium Silicate,**" by Stephen Brunauer, J. C. Hayes and W. E. Hass.

Reprinted from *The Journal of Physical Chemistry,* **58,** 279 (1954).

Bulletin 49—"**Void Spacing as a Basis for Producing Air-Entrained Concrete,**" by T. C. Powers.

Reprinted from *Journal of the American Concrete Institute* (May, 1954); *Proceedings,* **50,** 741 (1954).

Bulletin 49A—**Discussion of the paper "Void Spacing as a Basis for Producing Air-Entrained Concrete,"** by J. E. Backstrom, R. W. Burrows, V. E. Wolkodoff, and Author, T. C. Powers.

Reprinted from *Journal of the American Concrete Institute* (December, Part 2, 1954); *Proceedings,* **50,** 760–1 (1954).

Bulletin 50—"**The Hydrates of Magnesium Perchlorate,**" by L. E. Copeland and R. H. Bragg.

Reprinted from *The Journal of Physical Chemistry,* **58,** 1075 (1954).

Bulletin 51—"**Determination of Sodium and Potassium Oxides in Portland Cement Raw Materials and Mixtures, and Similar Silicates by Flame Photometry,**" by C. L. Ford.

Reprinted from *Analytical Chemistry,* **46,** 1578 (1954).

Bulletin 52—"**Self Desiccation in Portland Cement Pastes,**" by L. E. Copeland and R. H. Bragg.

Reprinted from *ASTM Bulletin,* No. **204,** 34 (February, 1955).

Bulletin 53—"**Permeability of Portland Cement Pastes,**" by T. C. Powers, L. E. Copeland, J. C. Hayes, and H. M. Mann.

Reprinted from *Journal of the American Concrete Institute*, (November, 1954); *Proceedings*, **51**, 285 (1955).

Bulletin 54—"**Some Observations on the Mechanics of Alkali-Aggregate Reaction,**" by L. S. Brown.

Reprinted from *ASTM Bulletin*, No. **205**, 40 (April, 1955).

Bulletin 55—"**An Interpretation of Published Researches on the Alkali-Aggregate Reaction: Part 1—The Chemical Reactions and Mechanism of Expansion; Part 2—A Hypothesis Concerning Safe and Unsafe Reactions with Reactive Silica in Concrete,**" by T. C. Powers and H. H. Steinour.

Reprinted from *Journal of the American Concrete Institute* (February and April, 1955); *Proceedings*, **51**, 497, 785 (1955).

Bulletin 56—"**Comparison of Results of Three Methods for Determining Young's Modulus of Elasticity of Concrete,**" by R. E. Philleo.

Reprinted from *Journal of the American Concrete Institute* (January, 1955); *Proceedings*, **51**, 461 (1955).

Bulletin 57—"**Osmotic Studies and Hypothesis Concerning Alkali-Aggregate Reaction,**" by George J. Verbeck and Charles Gramlich.

Reprinted from *Proceedings, American Society for Testing Materials*, **55**, (1955).

Bulletin 58—"**Basic Considerations Pertaining to Freezing and Thawing Tests,**" by T. C. Powers.

Reprinted from *Proceedings, American Society for Testing Materials*, **55**, (1955).

Bulletin 59—"**New Study on Reactions in Burning Cement Raw Materials,**" by L. A. Dahl.

Reprinted from *Rock Products*, **58**, No. 5, 71; No. 6, 102; No. 7, 78 (1955).

Bulletin 60—"**Long-Time Study of Cement Performance in Concrete—Chapter 9. Correlation of the Results of Laboratory Tests with Field Performance Under Natural Freezing and Thawing Conditions,**" by F. H. Jackson.

Reprinted from *Journal of the American Concrete Institute* (October, 1955); *Proceedings* **52**, 159 (1956).

Bulletin 61—"**A Method for the Determination of the Cement Content of Plastic Concrete,**" by W. G. Hime and R. A. Willis.

Reprinted from *ASTM Bulletin* No. **209** 37 (October, 1955).

Bulletin 62—"**Investigation of the Franke Method of Determining Free Calcium Hydroxide and Free Calcium Oxide,**" by E. E. Pressler, Stephen Brunauer and D. L. Kantro.

Reprinted from *Analytical Chemistry*, May, 1956.

Bulletin 63—"**Hydraulic Pressure in Concrete,**" by T. C. Powers.

Reprinted from *Proceedings, American Society of Civil Engineers*, **81**, 742 (July, 1955).

Bulletin 64—"**The Freezing and Thawing Test,**" by T. C. Powers.

Reprinted from *ASTM Report on Significance of Tests of Concrete and Concrete Aggregates*, 3rd. Edition, 1955.

Bulletin 65—"**The Stoichiometry of the Hydration of Tricalcium Silicate at Room Temperature: I—Hydration in a Ball Mill; II—Hydration in a Paste Form,**" by by Stephen Brunauer, L. E. Copeland and R. H. Bragg.

Reprinted from *The Journal of Physical Chemistry*, Vol. 60, p. 112 (January, 1956).